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SURFACE CHEMISTY AND STRUCTURAL EFFECTS IN THE STRESS CORROSION OF GLASS AND CERAMIC MATERIALS

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Preface

(Contract F49620-88-C-0074)

This report presents the work performed at The Pennsylvania State University during the period 1 May 1989 to 31 December 1989. The program was directed by Professor Carlo G. Pantano and graduate student Armando Gonzalez was co-investigator.

The Final Report (on Contract F49620-86-K-0005) submitted in August 1988 described the design and construction of an instrumental facility where the surface phenomena associated with fracture and slow crack could be studied. This Final Report concerns the use of that facility to evaluate mechanisms of crack growth in vacuum (see also Annual Report for the period 1 May 1988 to 30 April 1989).

The two chapters included in this report were submitted for publication to Applied Physics Letters (Fractoemission During Crack Propagation in Glass, submitted) and Journal of the American Ceramic Society (A Comprehensive Loaded Double Cantilever Beam Specimen, accepted).

FRACTOEMISSION DURING CRACK PROPAGATION IN GLASS

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ABSTRACT

The phenomena termed fractoemission was monitored in soda-lime-silica glass specimens during slow crack growth. No electron, ion, or photon signals were detected until crack velocities reached approximately 10^{-2}m/s. These observations suggest that the more intense fractoemissions observed during fast fracture are due to dissipation of the excess energy associated with unstable crack growth, but more significantly that fractoemissions are not fundamental to crack propagation in glass.

Fractoemission is a wide-ranging phenomena that has been observed in glasses, inorganic crystals, polycrystalline ceramics, elastomers, fiber-reinforced composites, and adhesives.[1-6] The study of fractoemission in fused silica and alkali-silicate glasses by Dickinson, et al.[1,2] has clearly demonstrated that a significant emission of neutral particles, charged particles (electrons and ions), and photons accompany the fracture event. The emission currents usually maximize upon the initiation of fracture, and decay over a period of milliseconds thereafter. In the case of the neutral and ionic particles, mass analysis has identified them to be constituents of the glass, e.g., O_2, Na, O^+, Na^+, Si^+ and SiO^+.

A model to explain the time dependent fractoemission intensity has been proposed by Dickinson.[6] The emission is described in a three step process:

(1) fracture produces highly reactive displaced species, x and y,

(2) diffusion limited mass transport brings these reactive species together, creating an excited intermediate, $(x+y) \rightarrow (x+y)^*$,

(3) this excited intermediate decays to produce energetic particles in the form of electrons, ions, neutrals, and photons.

In our laboratory, we are studying slow crack growth in vacuum, i.e., at pressures less than 4×10^{-5} Pa.[7-11] The measured crack velocities typically range between 10^{-10} m/s and 10^{-3} m/s and are controlled through the applied load. Not all materials exhibit slow crack growth in vacuum. It has been found that four very different glass systems (silicate, phosphate, fluoride, and chalcogenide), and four single crystals (out of eight evaluated) have been susceptible to slow crack growth in vacuum. The exact mechanism behind this phenomena is still in question.

If electron and ion emission is an integral part of the fracture process, its measurement during slow crack growth may lead to a better understanding of the physical processes associated with strain induced bond-breaking. Thus, the objective of these studies was to determine whether a relationship exists between the crack velocity, and the intensity, energy, or mass of the ejected particles. To date, there have been no reported attempts to measure fractoemissions during the stable, sub-critical propagation of a crack.

The experimental arrangement is shown in Figure 1. The test specimens were commercial soda-lime-silica glass microscope slides mounted in a double cantilever beam configuration.[7] A groove, one-half the thickness of the slide, was machined along its center to guide the crack along the length of the specimen. The crack velocity was controlled by varying the applied load through a push-rod fastened to a micrometer driven feedthrough. The specimen fixture was held in an all-metal vacuum chamber where the pressure was held to 4×10^{-5} Pa. The charged particle emissions were monitored during crack growth using an electron multiplier (Galileo 4720) which was positioned one cm from the specimen. The entrance cone of the multiplier (3.8 cm diameter) was centered around the crack-tip, thus encompassing a solid angle of 112°. The multiplier was operated at + or - 2kv, yielding a gain of 10^8. The photon emissions were monitored using a photomutiplier tube (RCA 8852-RF) that was operated at 1kv.

In general, charged particle fractoemissions were **not** detected over the entire range of crack velocities (10^{-10} to 10^{-3} m/s). The background count rate was approximately 1 cps, and in the range 10^{-3} to 10^{-2} m/s of crack velocity, the signal increased to 15 cps. Also, any transient acceleration of the crack due to 'tapping' the specimen yielded a detectable signal. Of course, unstable (fast) fracture of the double cantilever test specimen created the usual fractoemission signal.

Since the measurement of the photon emission had to be conducted in total darkness, the crack could not be directly observed to determine its velocity. In this case, the load on the specimen was slowly increased until complete failure occurred. Again, only during the catastrophic failure was there any detectable photon signal. (The catastrophic failure was audible, so correlation with the peak in the photon signal was easily confirmed.)

This study of fractoemission during slow crack growth was a logical extension of the fast fracture studies conducted by Dickinson and co-workers.[1,2] The fact that particle emissions were not detected over such a wide range of crack velocities is significant, but several factors must be considered in the interpretatation. It is especially important to recognize at the onset of this discussion that in the fast fracture studies, the fracture surfaces (and hence the broken bonds) are

created at nearly 1000 m/s, and moreover are almost instantaneously separated. In the present case, the rate of bond-breaking is not only slow, but the fracture surfaces are situated within atomic dimensions of one another throughout the course of the slow crack growth experiment. These differences can have some important effects.

First, consider the effect of crack velocity; that is, the rate of bond cleavage. If it is assumed that only one charged particle is created per broken bond, and all of these are detected, then currents in the range nA's to mA's are expected for crack velocities between 10^{-10} and 10^{-3} m/s. These currents are certainly within the detection limits of the channel electron multiplier. And even if only a small fraction of the broken bonds create charged particles, detectable signals are expected over most of the crack velocity range. This estimate also explains the readily detectable fractoemission signals observed in fast fracture experiments where currents could exceed mA's.

Next, consider the geometry during slow crack growth and its effect upon the detection of the fractoemissions. It seems likely that many of the charged particles ejected during slow crack growth would not be able to escape the confines of the crack tip. This is undoubtedly the reason why the fractoemission signals are low even at the highest crack velocities; i.e., only the particle emissions at the edge of the crack were detected. But this does not explain the absence of photon signals. These signals are readily transmitted through the glass, and nonetheless they were detected only upon catastrophic fracture of the glass. Altogether, it seems that problems associated with the limited escape of fractoemissions do exist during slow crack growth experiments, but the cannot explain entirely, the experimental results of this study.

Thus, the fundamental origin and mechanisms of the fractoemissions must be reconsidered. These are not completely understood, in general, but according to Dickinson[6] are associated with the creation of excited intermediates on the fracture surfaces due to the reactive broken bonds. Presumably, these intermediate species can create energetic fractoemissions through a variety of de-excitation processes. During the slow propagation of a crack, however, the number and/or reactivity of the broken bonds may be reduced through deformation or reconstruction processes at the advancing crack tip. It is also possible that the close proximity of the fracture surfaces provides

more efficient mechanisms for passivation of the broken bonds and/or for de-excitation of any intermediates formed. The most obvious effect would be 'charging' of the fracture surfaces due to their rapid separation in the case of the fast fracture versus the possibility for charge exchange or charged particle recombination across the closely-spaced fracture surfaces in the case of slow crack growth. This could, in principle, explain the lack of fractoemission signals during slow crack growth, and as such, cannot be excluded as a plausible interpretation of the observations.

Nonethless, we believe that the correct interpretation of the apparent fractoemission 'threshold' concerns the total amount of energy used to fracture the specimen versus the minimum amount which is necessary to cause fracture. In fast fracture , the amount of stored mechanical energy at the onset of fracture exceeds the minimum value necessary to create new surface. In the typical fast fracture experiment,[1,2] a bend specimen is loaded to failure; the crack accelerates to a terminal velocity, and for this reason, fast fracture is inherently unstable. In theory, at least, slow fracture in vacuum requires only enough energy to balance the creation of new surface; the stability in slow crack propagation is provided by the double-cantilever type specimens. This point is quantitatively verified in fracture mechanics measurements; the fracture energy of soda-lime-silica glass is 4.5 J/m^2, whereas its slow crack growth in vacuum occurs at a level of less than 3.5 J/m^2, a difference of 1 J/m^2.

It is proposed that fractoemissions occur only when the mechanical energy delivered to the fracture specimen exceeds the minimum energy necessary to create the fracture surface. The excess energy required for a given fractoemission would be defined by the type of particle (electron, ion, neutral, or photon), and its energy state. Consider, for example:

$$Si \rightarrow Si^+ + e^-$$

where Si^+ and e^- are two of the fractoemissions observed in the fast fracture experiments.[1,2] The enthalpy of formation for this ionization is about $2x10^{-18}$ J/ion. The **minimum** energy delivered to the specimen in the fast fracture experiments can be calculated using the fracture energy for soda-lime-silica glass(4.5 J/m^2). Thus, the total energy delivered to the 4 mm rods used in the fast

fracture experiments[1,2] is found to be at least 56×10^{-6} J. A slow crack propagation in vacuum would expend only 44×10^{-6} J in a specimen of this size. The excess energy available in the fast fracture case, therefore, is 12×10^{-6} J and this is sufficient to ionize 6×10^{12} Si species! This corresponds to only about 3% of the total number of fracture surface species, but nonetheless represents a large number of particles that could **not** be created during a slow fracture. Of course, this is a crude estimate. It underestimates the total energy available in the typical fast fracture experiment, and in this sense, it is conservative. On the other hand, it overestimates the amount of this excess energy that would be available to ionize Si because it does not account for the creation of the 'free' Si, nor the many other particles, neutral and charged, that are observed during fracture. However, this is not a severe assumption because Na, for example, produces a more intense fractoemission than Si, and it would use much less energy to reach the 'free' state or the ionic state. Altogether, the estimate does provide semi-quantitative verification of the proposed hypothesis; and that is the fact that even the **minimum** 1 J/m^2 difference in fracture energy between fast and slow fracture provides sufficient energy to ionize many fracture surface species. We emphasize, further, that this minimum energy difference has been greatly exceeded in most of the fast fracture studies of fractoemission reported in the literature, and in fact that the dependence of the fractoemission intensity upon the energy stored in the specimen at fracture has already been demonstrated (see Figure 6 in Reference 1).

In summary, it was found that there are no measurable particle emissions during slow crack growth in soda-lime-silica glass. Even at the apparent threshold velocity of 10^{-3}-10^{-2} m/s, the fractoemission signal levels are much lower than in the fast fracture experiments. These differences can be explained in terms of the excess energy which is necessary to achieve fast (unstable) fracture. We conclude that particle emission is not fundamental to the bond cleavage that occurs during crack propagation.

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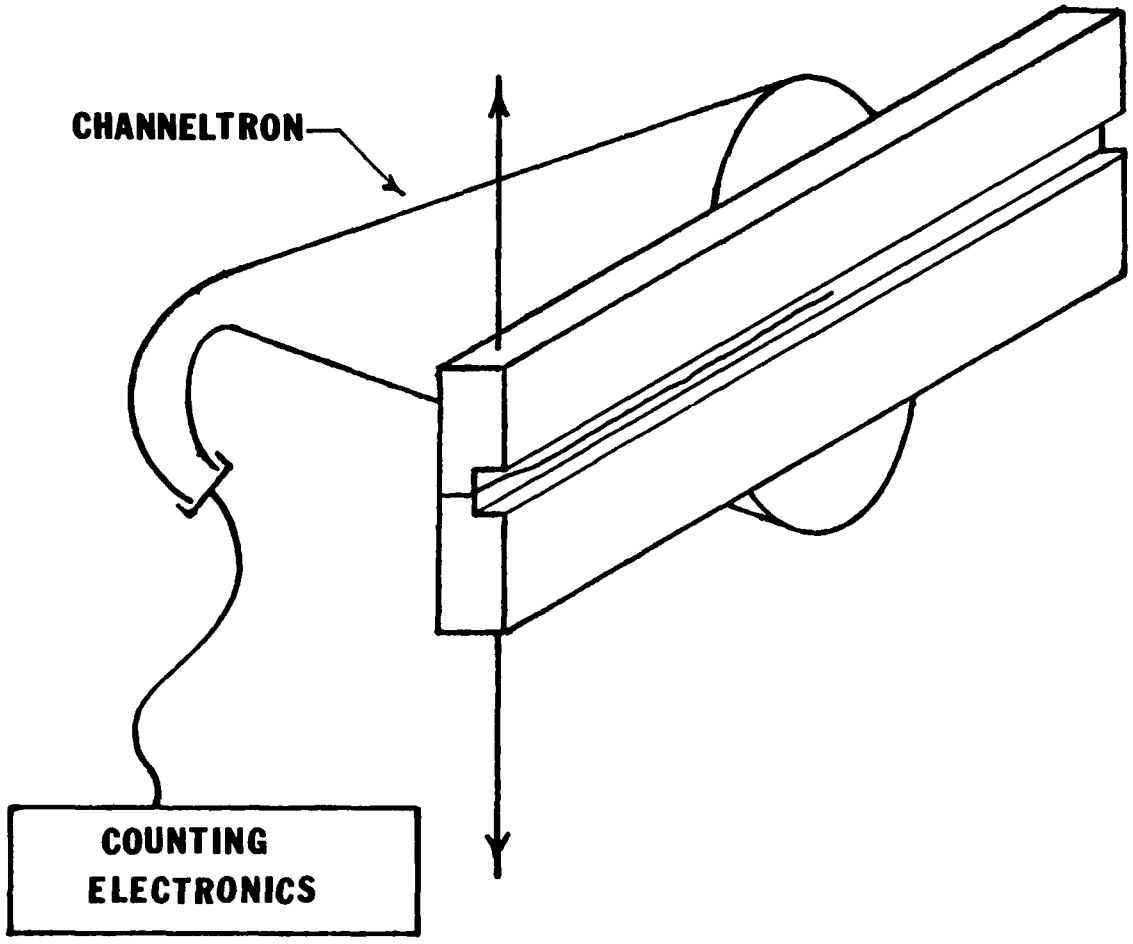
Figure 1. Double cantilever beam specimen and electron multiplier arrangement employed inside of vacuum chamber.


CHANNELTRON
COUNTING
ELECTRONICS

A Compression Loaded Double Cantilever Beam Specimen

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In crack propagation studies, double cantilever beam specimens are typically loaded in tension or by an applied moment. A method of compression loading is described in which the stress intensity K_I decreases with crack length. This new arrangement offers added crack stability over other techniques, as well as a convenient method of loading.

KEY WORDS:

double cantilever beam specimen, fracture, crack propagation, stress intensity, crack velocity

* Member of the American Ceramic Society

The double cantilever beam (DCB) specimen is used extensively to determine the fracture toughness, K_{IC}, and crack growth susceptibility of brittle materials [1-3]. There are two common methods of loading this specimen, and here, a third method is suggested which may be advantageous in certain applications.

In a conventionally loaded DCB specimen a tensile load is applied to the specimen as shown in Figure 1a. The resulting stress intensity at the crack tip is given by [2]:

$$K_I = Pc/(bh^3t)^{1/2} [3.467 + 2.315h/c], \quad (1)$$

where these terms are defined in Figure 1a. Because the stress intensity depends on the total crack length, c, K_I will increase for a given applied load as the crack propagates. So during slow crack growth, both the load and the crack length must be carefully monitored to avoid catastrophic failure caused by an accelerating crack.

An alternative loading method developed by Freiman et al., results in a stress intensity at the crack tip which is independent of crack length, and hence is better suited for crack propagation measurements [4]. In this so called constant moment DCB, the specimen is loaded through a pure moment as the name implies. This is generated by a force-couple acting on loading arms which are fastened to the specimen (see Figure 1b). The resulting expression for K_I is:

$$K_I = PL(3)^{1/2} / (bh^3t)^{1/2}, \quad (2)$$

which is independent of crack length, and for a given specimen K_I is directly proportional to the applied load, P.

In our laboratory we are studying the slow crack growth of various glasses and single crystals, in vacuum. A DCB configuration was favored for these experiments for two reasons; first, most existing slow crack growth data on brittle materials has been collected using this technique and secondly, direct observation of crack motion would be possible by placing a viewport on the vacuum chamber. Nevertheless several obstacles arose.

The usable volume of the vacuum chamber was small (5 cm x 5 cm x 5 cm), so there was not sufficient room to easily accommodate a constant moment loading arrangement. The alternative was to use a tensile DCB specimen (see Figure 1a) which is more compact, but in the present application could easily result in premature specimen failure due to its intrinsic instability. Under vacuum, crack growth exponents, or N values, may range from 50 to 1000, so crack velocities are a very strong function of the applied stress intensity. Because K_I increases monotonically as the crack grows, the applied load must be adjusted in order to prevent catastrophic failure. With such large crack growth exponents occurring in vacuum, continuous vigilance would be required to control the crack velocity with this type of specimen.

A solution to these complications was achieved by changing the orientation of the loading arms used in the applied moment DCB specimen to that shown in Figure 1c. Placing the arms parallel to the specimen and loading in compression produces both a closure force and an opening moment on the crack [5]. By linear

superposition, K_I for this new loading may be obtained by adding the two previous stress intensity solutions (equations 1 and 2). Since equation 1 is for tensile loading the sign must be changed because the applied load, P is now compressive. So for the new configuration the solution for K_I by superposition of stress intensities is:

$$K_{compression} = K_{constant\ moment} - K_{tensile} ,$$

$$K_{compression} = [P/(bh^3t)^{1/2}]\ [L(12)^{1/2} - 3.467c - 2.315h] , \quad (3)$$

and now K_I decreases as the crack extends. It should be emphasized that this solution is the sum of two existing solutions for the crack tip stress intensity factor, and as such it did not have to be solved from first principles.

Data obtained thus far using this technique show excellent agreement with that obtained by the constant moment loading method for a soda-lime silicate glass (see figure 2). Within the scatter of the data no systematic differences are evident. Data for a soda silicate glass collected by Simmons and Freiman [6] also match closely with the present results, further establishing the validity of this new loading method.

In our situation several advantages were gained with this loading arrangement. First, the specimen and loading arms formed a compact package which could easily be inserted and withdrawn from the vacuum chamber. Secondly, stability was insured as K_I now decreased with crack extension. If the specimen was inadvertently overloaded, the crack would arrest after extending less than 5 mm,

and the experiment could continue. Finally, a simple micrometer-driven pushrod could be used to load the sample inside the vacuum chamber. The load was measured by strain gages applied to one of the loading arms.

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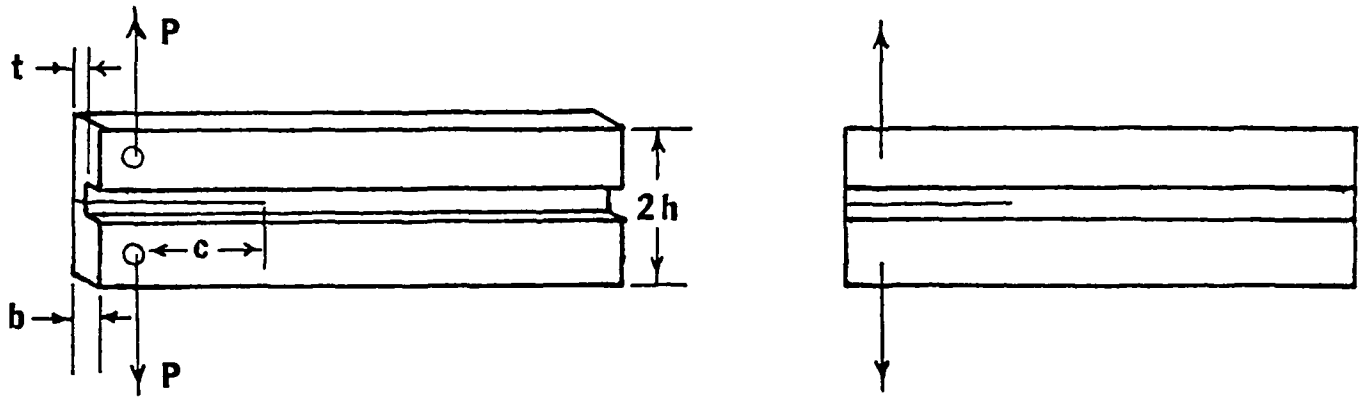
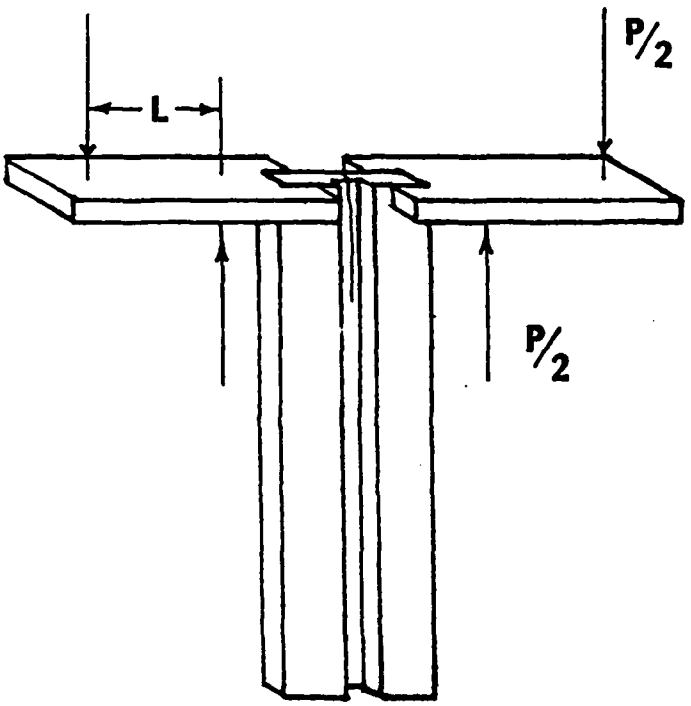
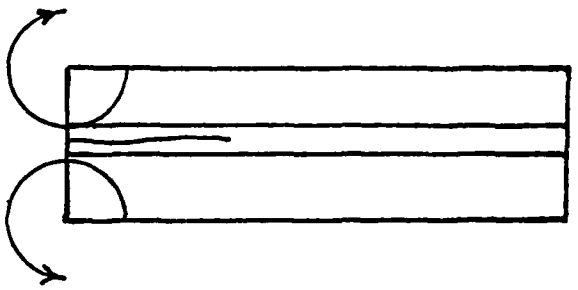
Figure 1) The DCB specimen and resultant forces for three different loadings; a) tensile, b) constant moment, and c) compression.



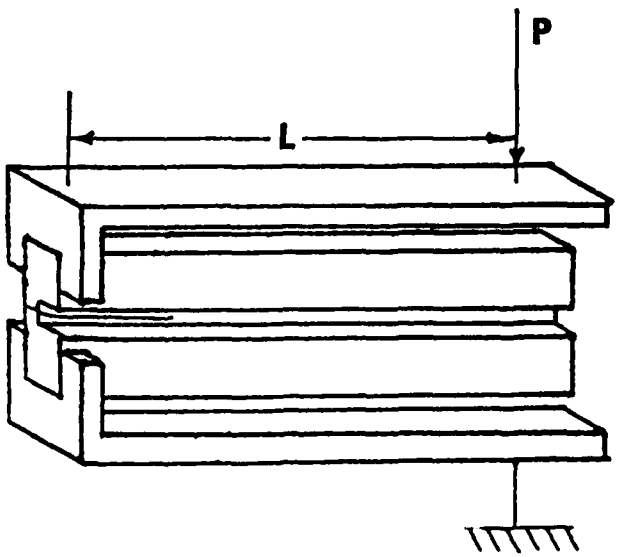
(a)

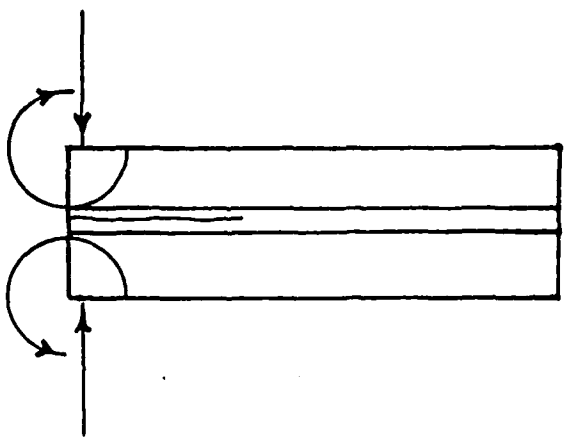
P = load
c = crack length
b = thickness
t = thickness at groove
2h = specimen height
L = moment arm





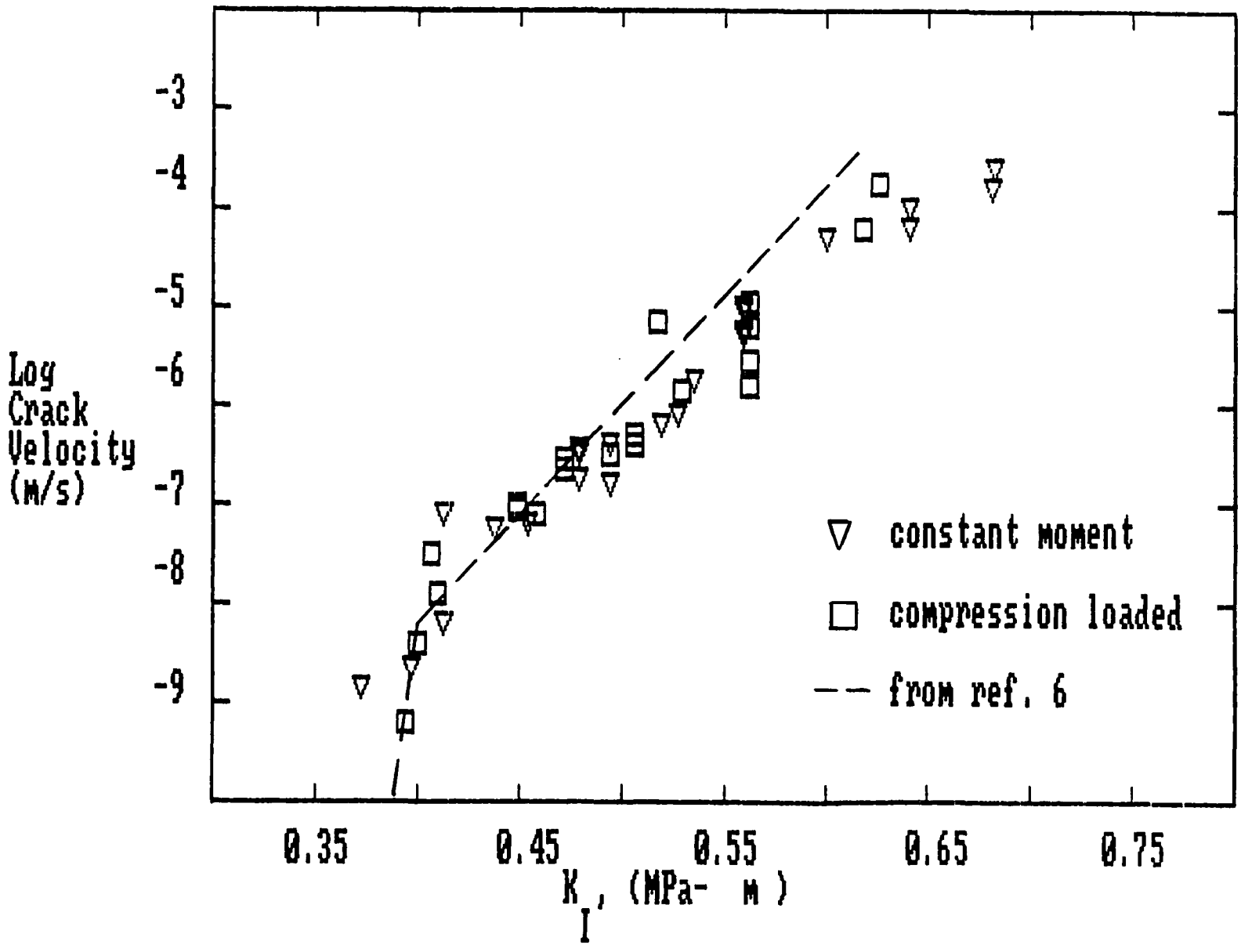
(b)





(c)

Figure 2) Crack velocity - stress intensity data for soda-lime silicate glass collected using compression and constant moment loaded DCB specimens. The results for a soda silicate glass obtained using a constant moment DCB technique (from ref. 6) are also shown for comparison.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Crack
Velocity
(m/s)
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-4
-5
-6
-7
-8
-9
0.35
0.45
0.55
0.65
0.75
K , (MPa- m)
I
constant moment
compression loaded
from ref. 6